Effect of excess lead and bismuth content on the electrical properties of high-temperature bismuth scandium lead titanate ceramics

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Aeronautic and aerospace applications require piezoelectric materials that can operate at high temperatures. The air-breathing aeronautic engines can use piezoelectric actuators for active combustion control for fuel modulation to mitigate thermo-acoustic instabilities and/or gas flow control to improve efficiency. The principal challenge for the insertion of piezoelectric materials is their limitation for upper use temperature and this limitation is due low Curie temperature and increasing conductivity. We investigated processing, microstructure and property relationship of (1-x)$BiScO_3$-(x)$PbTiO_3$ (BS-PT) composition as a promising high temperature piezoelectric. The effect of excess Pb and Bi and their partitioning in grain boundaries were studied using impedance spectroscopy, ferroelectric, and piezoelectric measurement techniques. Excess Pb addition increased the grain boundary conduction and the grain boundary area (average grain size was 24.8µm, and 1.3µm for compositions with 0at.% and 5at.% excess Pb, respectively) resulting in ceramics with higher AC conductivity (tan δ= 0.9 and 1.7 for 0at.% and 5at.% excess Pb at 350 ^oC and at 10kHz) that were not resistive enough to pole. Excess Bi addition increased the resistivity (ρ= 4.1x10^{10} Ω.cm and 19.6 x10^{10} Ω.cm for compositions with 0at.% and 5at.% excess Bi, respectively), improved poling, and increased the piezoelectric coefficient from 137 to 197 pC/N for 5at.% excess Bi addition. In addition, loss tangent decreased more than one order of magnitude at elevated temperatures (>300 ^oC). For all compositions the activation energy of the conducting species was similar ($\approx$ 0.35-0.40 eV) and indicated electronic conduction.

Effect of excess PbO and Bi_2O_3 content on the electrical properties of high-temperature $BiScO_3$-$PbTiO_3$ ceramics

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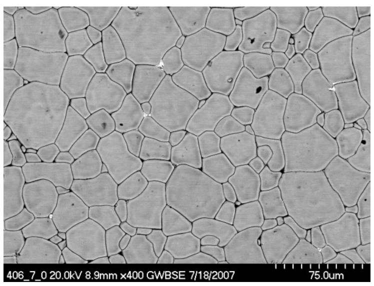

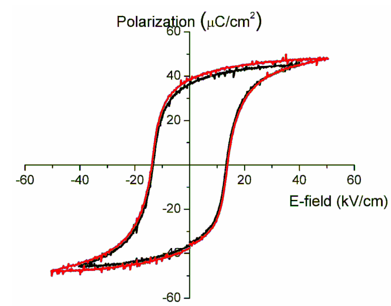

Objective

Development of high-temperature piezoelectric actuators for aeronautics and aerospace applications.

Applications

- Actuators for Aerospace and Aeronautics
  - Fuel modulation, valves, micro-positioning devices, MEMS, active damping and energy harvesting.
- Sensors
  - Pressure sensors, passive damping

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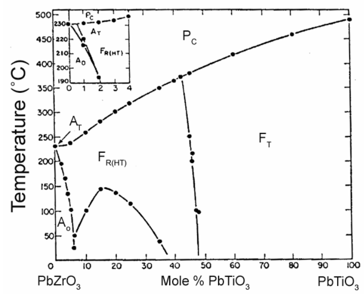
Challenges for High Temperature

- Trade off between T_C and d_{33}
- Conductivity at elevated temperatures

	T_{limit} (°C)/(°F)	d_{33} (pC/N)
PZT Type II (PZT 5A)	350 / 662	374
PMN-PT single crystals	90 / 194	>2000
$BiScO_3$-$PbTiO_3$	450 / 842	401
$La_3Ga_{5.5}Ta_{0.5}O_{14}$ single crystal	N/A	7
$Na_{0.5}Bi_{4.5}Ti_4O_5$	650 / 1202	19
$La_2Ti_2O_7$	1482 / 2700	16



B. Jaffe, W. R. Cook and H. Jaffe, Piezoelectric Ceramics, Academic Press, New York, 1971.

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Processing of BS-PT

Raw materials (Bi_2O_3, PbO, Sc_2O_3, TiO_2)

↓

Ball milling (15hrs)

↓

Drying (stirred)

↓

Calcination (750°C, 3hrs, 5°C/min), in air

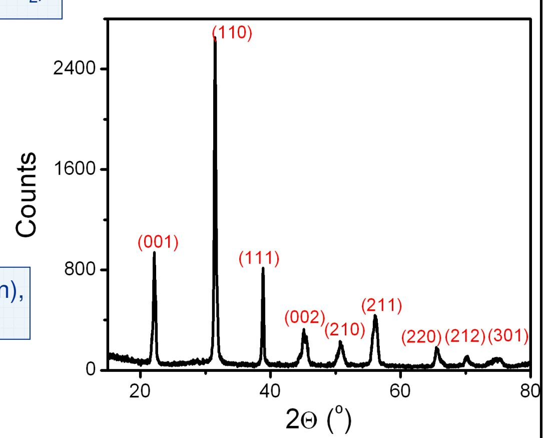
↓

Ball milling (6hrs)

↓

Pressing → Sintering (1100°C, 1hr, 5°C/min), in air

Excess addition → Ball milling (6hrs)



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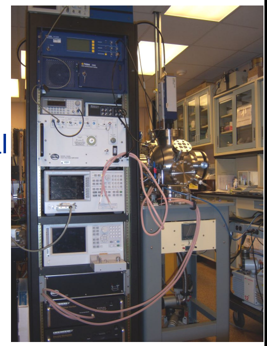
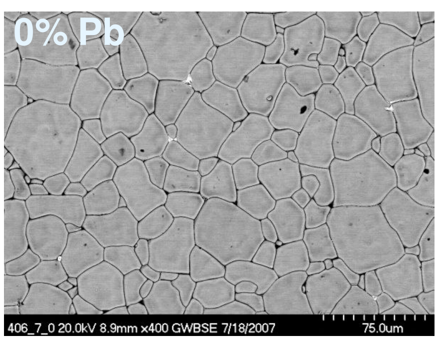
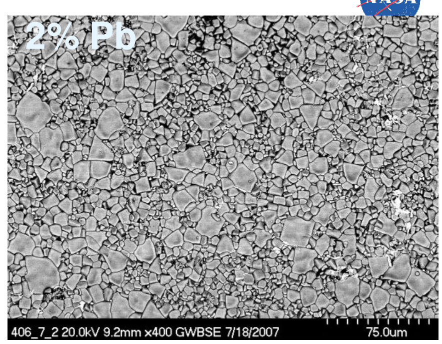
Electrical characterization

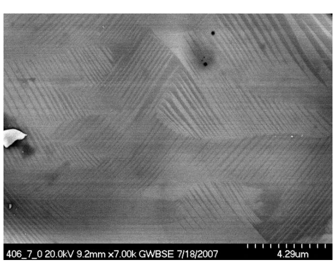


- Impedance measurements *(Solartron and HP Agilent)*
  - 1Hz-1MHz, Room temperature to 1000 ^{o}C.
  - 40Hz-110MHz, Room temperature to 600 ^{o}C.
  - 1Mhz-3Ghz, Microwave range
    (Determination of electrical, dielectric and electromechanical properties)
- Ferroelectric measurements *(Radiant Technologies)*
  - Bipolar, unipolar loops, leakage (up to 10,000V)
- Piezoelectric measurements
  - Laser dopplermeter *(Polytech)* coupled with a signal generator and a high power amplifier (up to 10,000V)
  - PhotonicTM sensor *(MTI technologies)* coupled with Radiant
  - Berlincourt d_{33} -meter

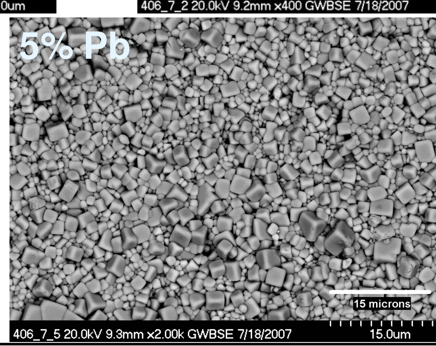
Effect of Pb on microstructure







0% Pb



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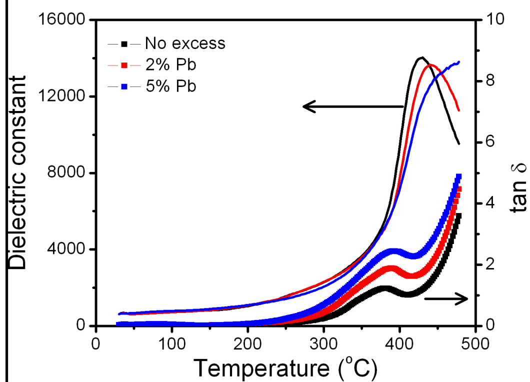
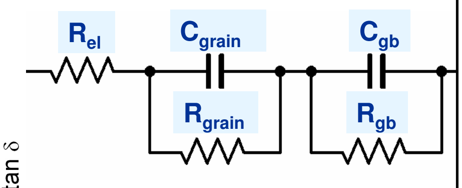
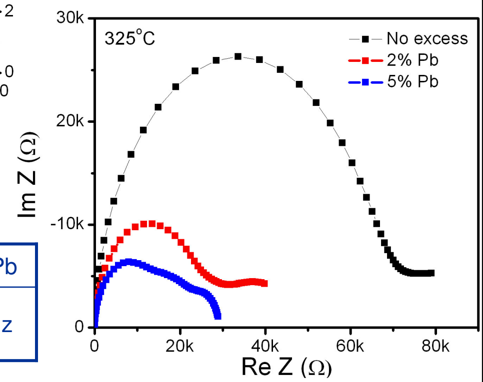
Effect of Pb in BS-PT



10 kHz, 0.5 V/mm ac, in air

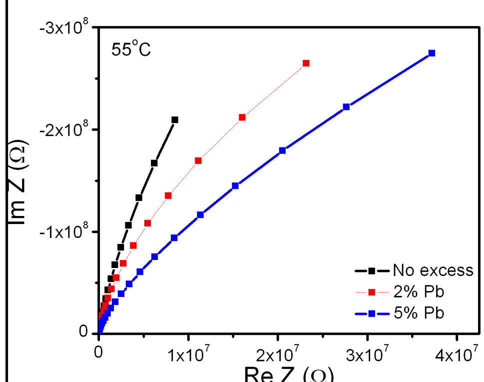


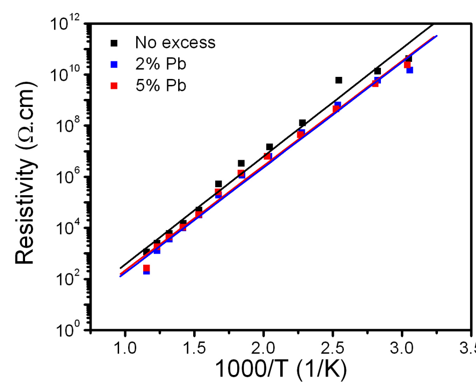
Grain boundary contribution



	0% Pb	2% Pb	5% Pb
Relaxation frequency	800 Hz	3 kHz	5 kHz

Effect of Pb in BS-PT





	ρ_{grain} (Ω.cm)	Dielectric constant, K_{grain}	E_{ac} (ev)
No excess	4.1×10^{10}	1085	0.36
2%Pb	2.4×10^{10}	805	0.35
5%Pb	1.4×10^{10}	727	0.35

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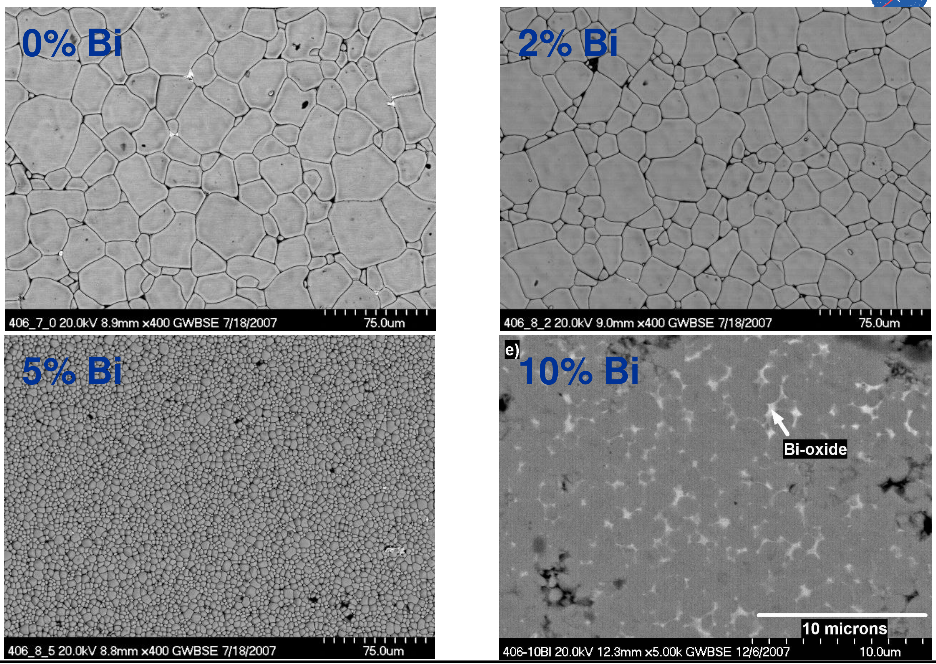
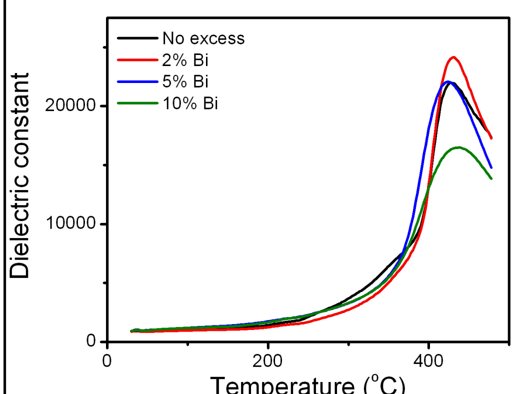
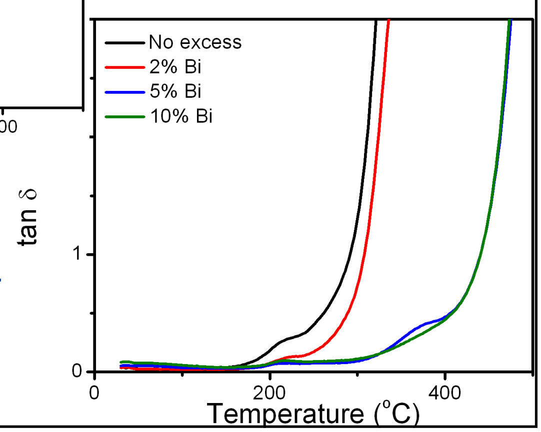
Effect of Bi on microstructure



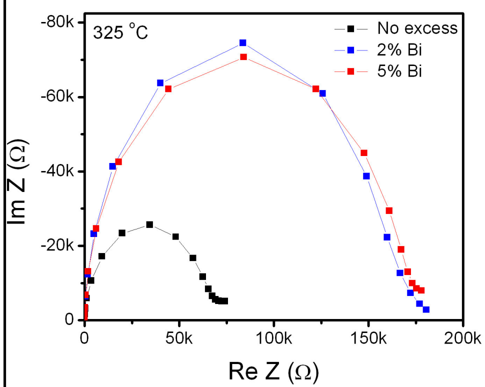
Effects of Bi in BS-PT

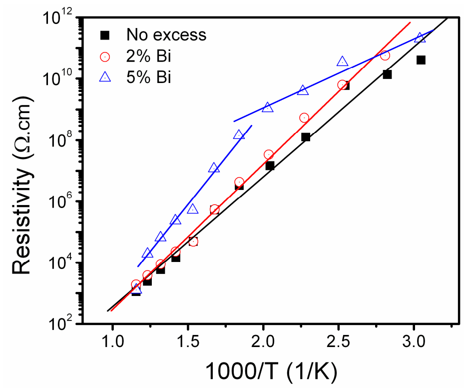


1 kHz, 0.5 V/mm ac, in air



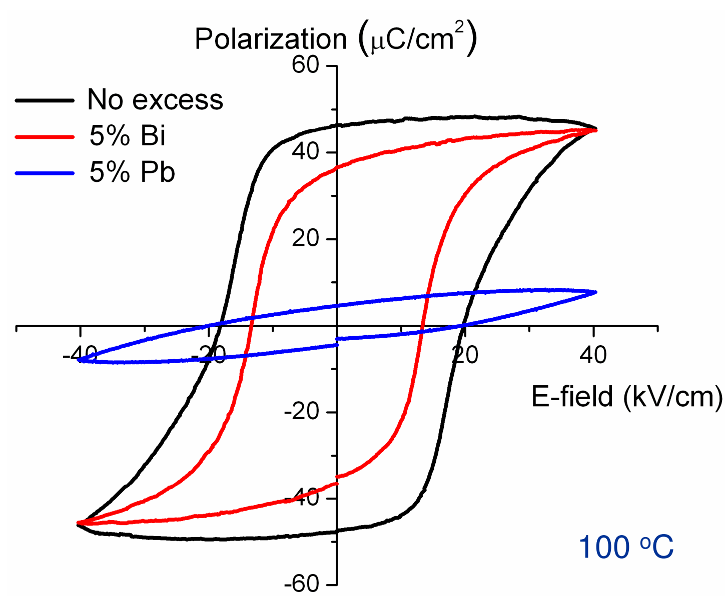
Effect of Bi in BS-PT

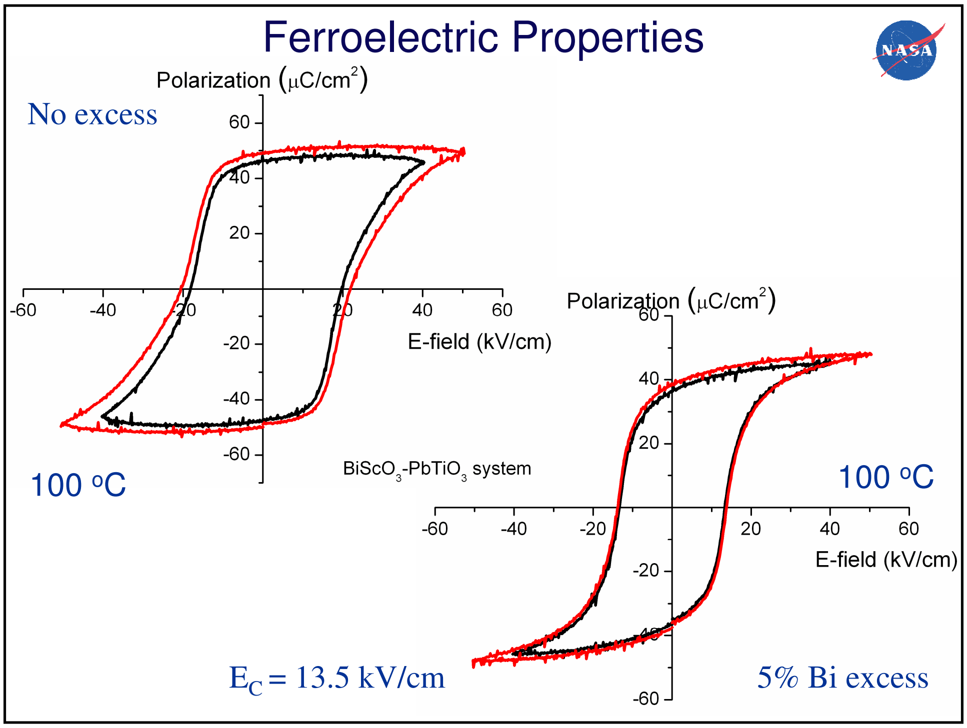


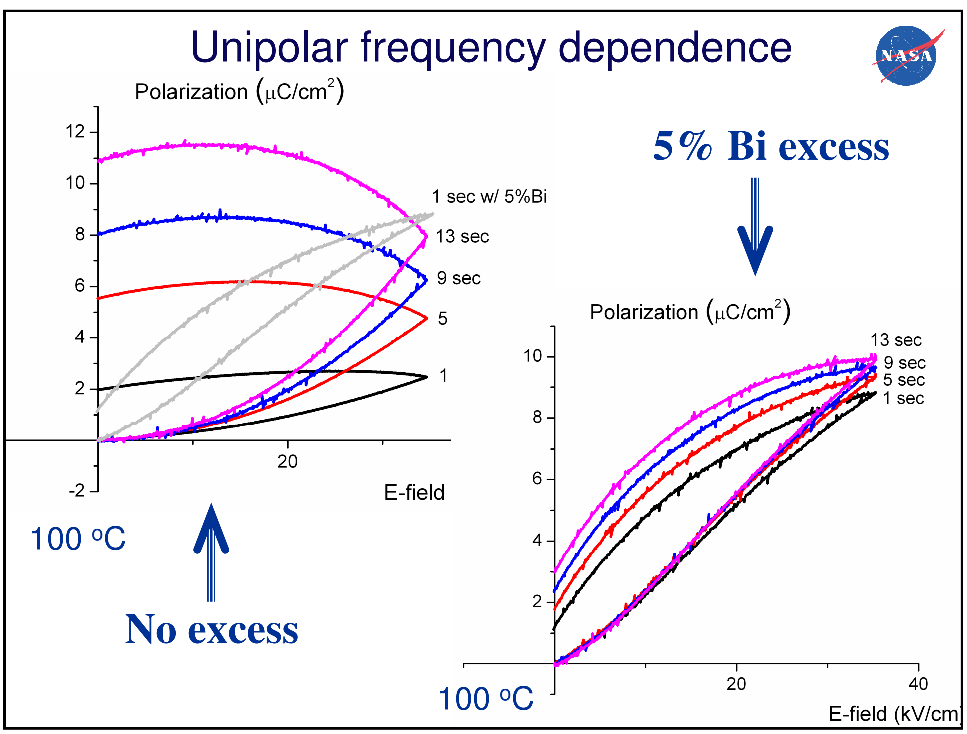


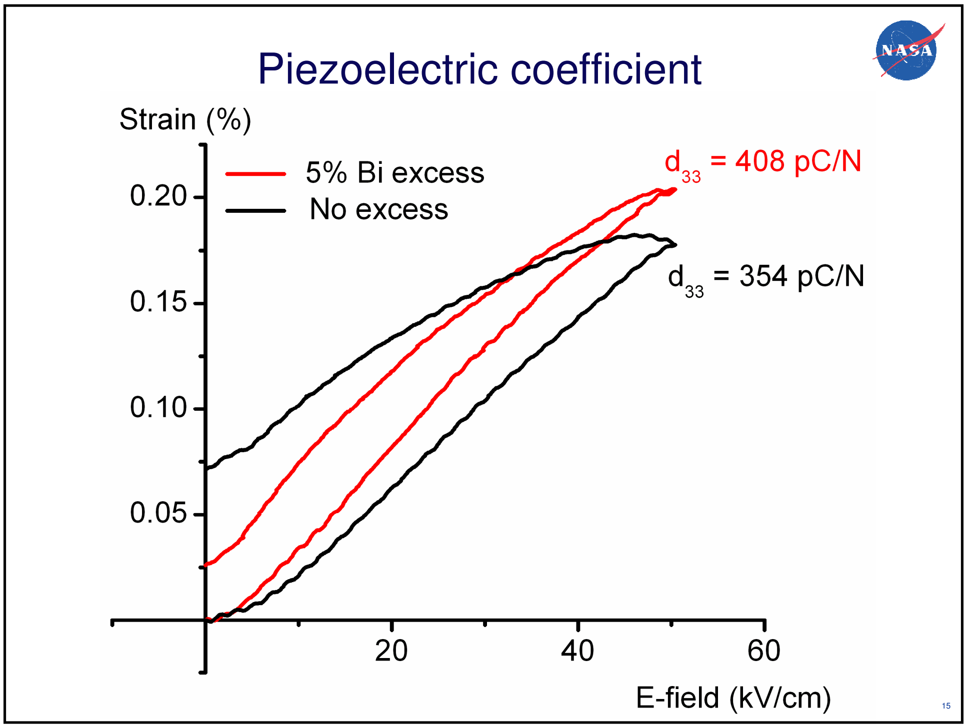
	ρ_{grain} (Ω.cm)	Dielectric constant, K_{grain}	Relaxation freq.	E_{ac} (ev)
No excess	4.1×10^{10}	1085	800 Hz	0.36
2% Bi	4.9×10^{10}	1104	400 Hz	0.40
5% Bi	19.6×10^{10}	1402	200 Hz	0.20, 0.59

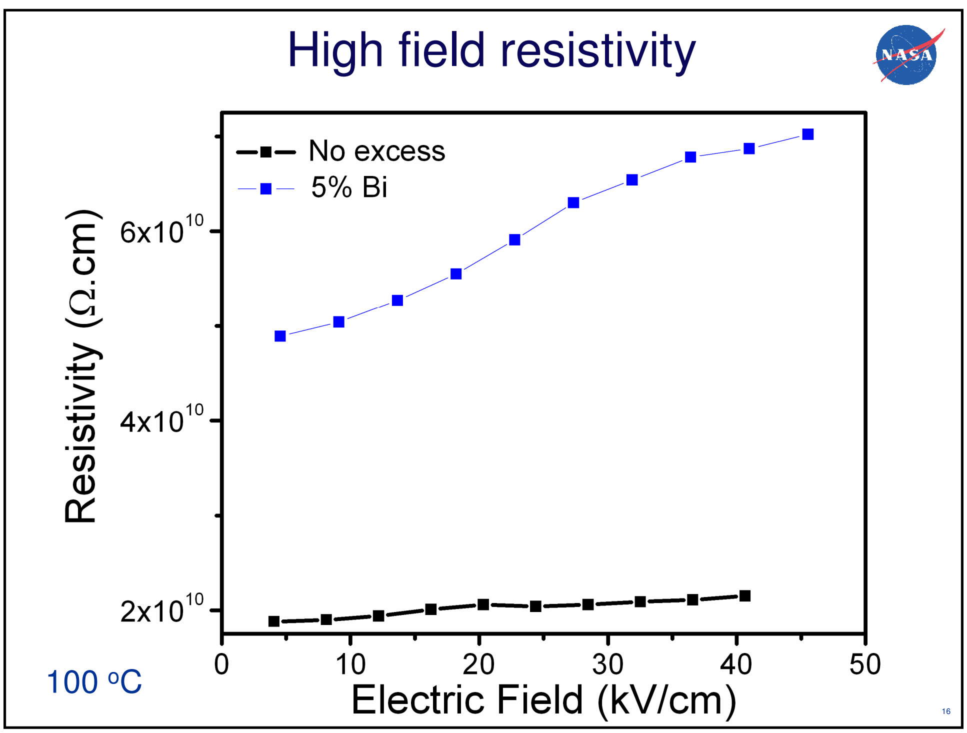
Ferroelectric and piezoelectric properties




Ferroelectric Properties
Polarization (μC/cm2)
No excess
60
40
20
-20
-40
-60
-60
-40
-20
20
40
60
E-field (kV/cm)
100 °C
BiScO3-PbTiO3 system
Polarization (μC/cm2)
60
40
20
-20
-40
-60
-60
-40
-20
20
40
60
E-field (kV/cm)
100 °C
EC = 13.5 kV/cm
5% Bi excess


Unipolar frequency dependence
Polarization (μC/cm2)
12
10
8
6
4
2
-2
20
E-field
1 sec w/ 5%Bi
13 sec
9 sec
5
1
100 °C
No excess
5% Bi excess
Polarization (μC/cm2)
10
8
6
4
2
20
40
E-field (kV/cm)
13 sec
9 sec
5 sec
1 sec
100 °C


Piezoelectric coefficient
Strain (%)
5% Bi excess
No excess
d_{33} = 408 pC/N
d_{33} = 354 pC/N
0.20
0.15
0.10
0.05
20
40
60
E-field (kV/cm)
15


High field resistivity
No excess
5% Bi
Resistivity (Ω.cm)
6x10^10
4x10^10
2x10^10
0
10
20
30
40
50
Electric Field (kV/cm)
100 °C
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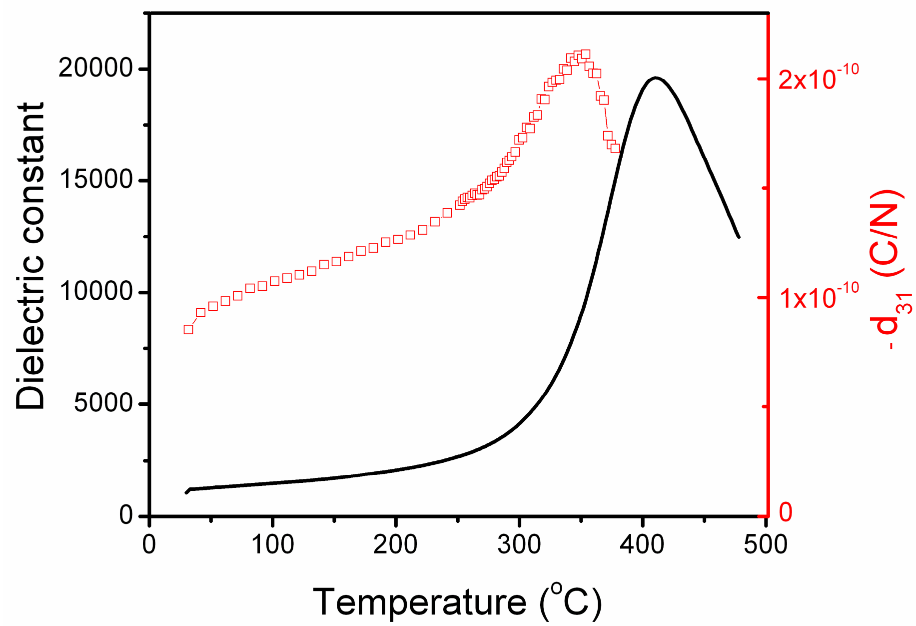
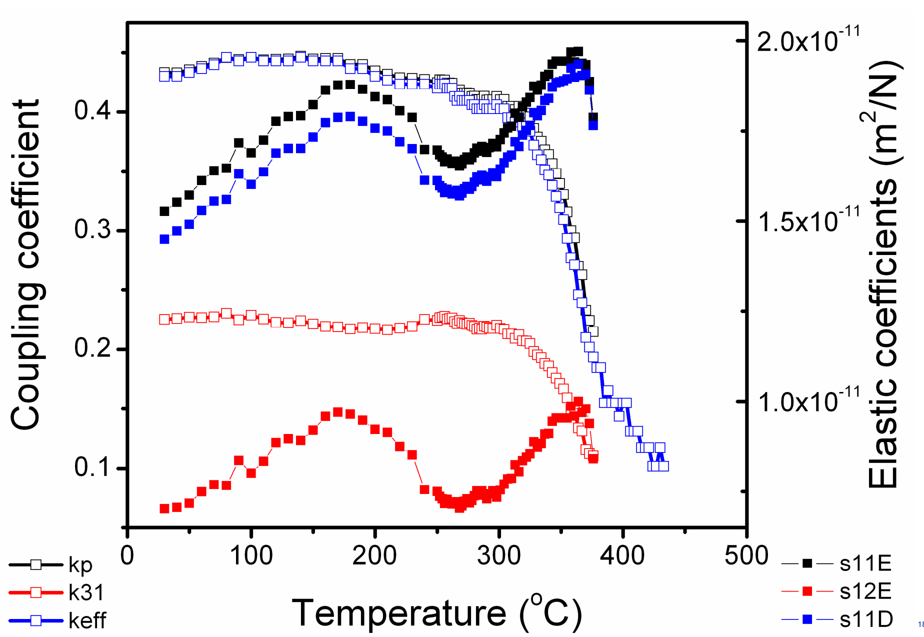
Resonance-Antiresonance Measurements



Resonance-Antiresonance Measurements



Summary

- $BiScO_3$-$PbTiO_3$ ceramics with T_C > 400°C has been successfully processed.
- Despite the increase in T_C, excess Pb addition increases both the bulk conductivity and the grain boundary contribution to conductivity at elevated temperatures.
- Conductivity at elevated temperatures, that limits the operating temperature for actuators, has been greatly reduced by excess Bi additions.
- Excess Bi doping improves poling conditions resulting in enhanced piezoelectric coefficient (d_{33} = 408 pC/N).

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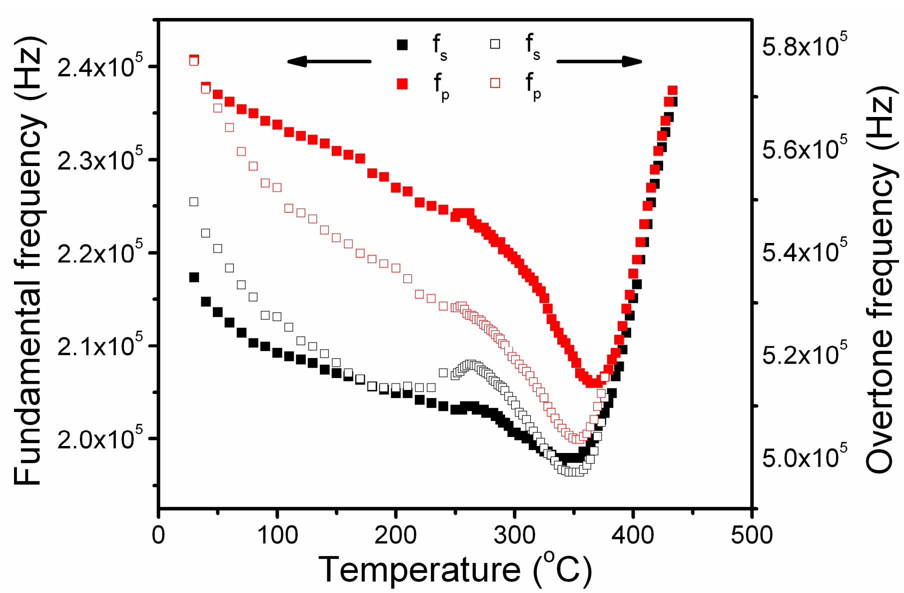
Resonance frequencies



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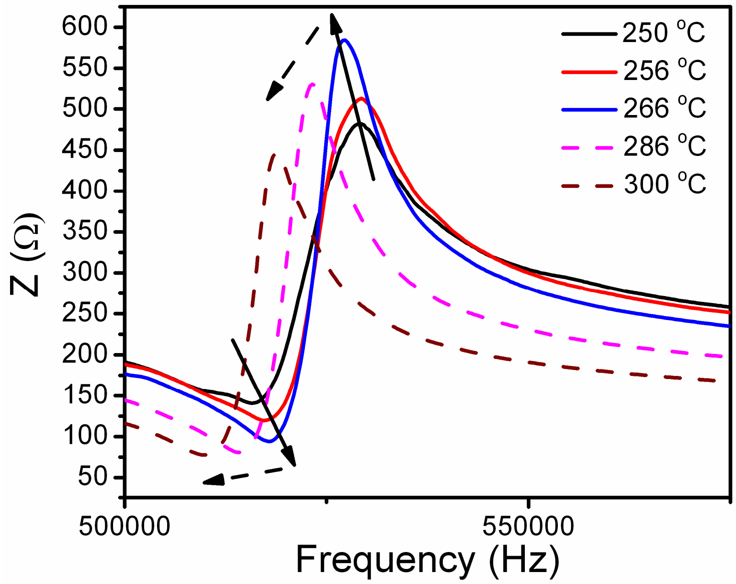
Resonance frequencies



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ICP

	Bi/ (Bi+Pb)	Pb/ (Bi+Pb)	Sc/ (Sc+Ti)	Ti/ (Sc+Ti)	O/ (Bi+Pb)	O/ (Sc+Ti)	O[1]
Calcined	0.372	0.628	0.358	0.642	2.515	2.411	2.865
Sintered	0.369	0.631	0.360	0.640	2.624	2.563	2.845

[1] Last column shows oxygen measured by the Oxygen Determinator. Three repeats were done on each powder sample. Due to the high oxygen content the sample size taken was around 5mg. The accuracy was estimated to be ± 0.25wt%.

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Impedance calculations

Composition	Grain size (μm)	ρ_{grain} (Ω.cm) at 55 °C	K_{grain} at 55 °C	Relax.freq. (Hz) at 325 °C	E_{ac} (eV) from ρ	E_{ac} (eV) from τ
No excess	24.8	4.1×10^{10}	1085	800	0.36	0.36
2% Pb	5.6	2.4×10^{10}	805	3000	0.35	0.32
5% Pb	1.3	1.4×10^{10}	727	5000	0.35	0.33
2% Bi	18.6	4.9×10^{10}	1104	400	0.40	0.40
5% Bi	3.35	19.6×10^{10}	1402	40	0.20 0.59	0.57

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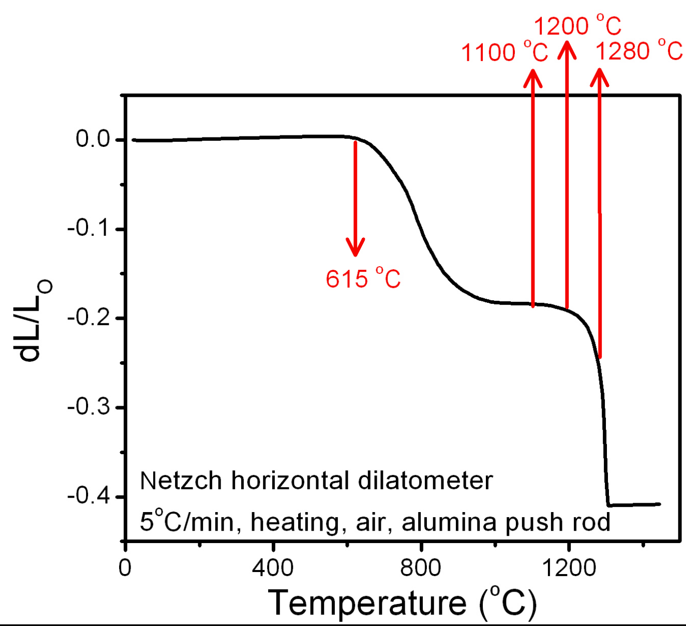
Sintering Conditions for BS-PT



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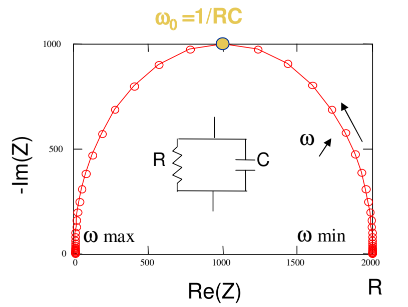
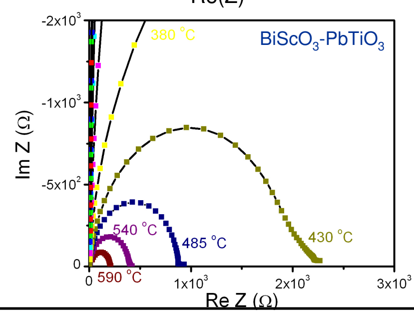
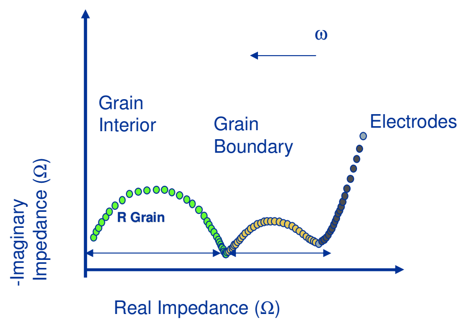
Impedance Spectroscopy

Conductivity - Grain/Grain Boundary







R // C : Resonance frequency ω_0 =1/RC

conduction: grain ≠ grain boundary

ω_0 grain boundary << ω_0 grain-Low T

ω_0 grain boundary ~ ω_0 grain-High T